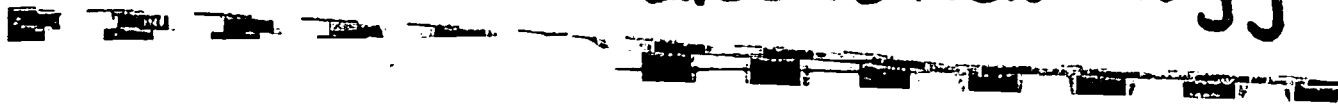


Electrotechnology



ELECTROTECHNOLOGY

Electrolysis is used both for extraction (electrowinning) and for refining (electrorefining) and in either case the electrolyte may be an aqueous solution or a mixture of fused salts. In extraction processes, the metal is in solution in the electrolyte from which it is plated on to the cathode, the anode being an insoluble conductor. In refining, the anode is the impure metal, the electrolyte is a solution of high electrical conductivity, and the cathode is of purer metal built up on a "starting sheet" or sometimes on a blank of another metal.

ELECTRODE TERMINOLOGY

Confusion often arises in the usage of the terms anode and cathode, and positive and negative, when referring to the electrodes of any electrochemical cell. In the following discussion the terms anode and cathode will be used in accordance with the strict definitions:

Anode - The electrode at which the electrons leave the cell.

Cathode - The electrode at which the electrons enter the cell.

These definitions apply both to electrolytic cells, where the current is being passed to the cell from an external source, and voltaic cells, which supply a current to an external circuit.

The arrangement in an electrolyte cell is shown in Figure 1(a). The cathode is connected to the negative terminal of the external supply. The arrangement in a voltaic cell is shown in Figure 1(b). In this type of cell, used as a source of e.m.f., the cathode is the positive electrode and the anode is the negative electrode. In any practical cell used as a source of power, the terms cathode and positive electrode are synonymous, as are the terms anode and negative electrode.

A secondary cell is a voltaic cell when it is supplying a current, and an electrolytic cell when it is being charged. The electrode which was the anode when the cell was discharging, becomes the cathode when the cell is on charge, and vice versa.

THERMODYNAMICS AND ELECTROCHEMICAL REACTIONS

In the Daniell cell the anode is zinc immersed in dilute sulphuric acid and the cathode is copper in dilute cupric sulphate solution, the two solutions being in electrical contact through a screen of porous pot.



and the net reaction is



If the electrodes are connected by a conductor of zero resistance there is no e.m.f. between them and the current passing can do no work. If however a potentiometer is interposed it will measure an e.m.f. under conditions of zero current which will have a maximum value characteristic of the net reaction under reversible conditions. The potentiometer makes its measurement by opposing the cell e.m.f. with a known variable e.m.f. until no current flows. If the measured value is E and the opposing e.m.f. is lowered to $(E - \Delta E)$ a small current will flow. If this is allowed to pass until 1 gm atom of zinc has dissolved and $2\mathfrak{F}$ coulombs of electricity will have passed and $2\mathfrak{F}(E - \Delta E)$ watt-seconds of electrical energy will have been generated. (Here, \mathfrak{F} is the Faraday, 96,500 coulombs per gram equivalent.) The corresponding free energy loss from the system will be at least $2\mathfrak{F}(E - \Delta E)$. If however the applied e.m.f. is raised to $(E + \Delta E)$ and one gram atom of zinc is deposited with the passage of 2 faradays of electricity, the amount of electrical energy supplied is $2\mathfrak{F}(E + \Delta E)$ watt-seconds and the free energy gain cannot exceed this amount of energy. If now ΔE is made to approach zero on each side, for the reaction to be carried out reversibly

$$\Delta G = -n\mathfrak{F}E \quad (4)$$

In general

$$\Delta G = \Delta G^\circ + RT \sum \ln a_i \quad (5)$$

(with log terms positive for products, negative for reactions).

If the cell is organized so that all components are in their standard states, the e.m.f. measured would be E° , related to the standard free energy according to

$$\Delta G^\circ = -n\mathfrak{F}E^\circ \quad (6)$$

Hence

$$E = E^\circ - \frac{RT}{n\mathfrak{F}} \sum \ln a_i \quad (7)$$

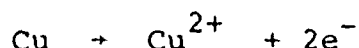
where

$$E^\circ = \frac{RT}{n\mathfrak{F}} \ln K_T \quad (8)$$

The standard states are usually the pure elements for the electrodes and the normal solution for the ions.

Any cell reaction can be split into two partial reactions (or groups of partial reactions) which can be assigned to the anode and the cathode respectively (Equations (1), (2) and (3)). Each of these has its free energy change and its corresponding electrode potential on a scale of volts in which the potential of the "standard hydrogen electrode" is zero. The e.m.f. of the cell is the sum of the anode potential and the cathode potential (care being taken that the sign of each corresponds to the direction in which the reaction goes).

The standard hydrogen electrode is in the form of a piece of platinum coated with colloidal "platinum black" which catalyses the reaction $H_2 = 2H^+$ between a stream of gaseous hydrogen at one atmosphere pressure and hydrogen ions in aqueous solution at normal concentration. Other more practical standard electrodes such as the calomel electrode are available as reference standards-"half cells" of known "half-cell potential" which can be coupled with half-cells of unknown potential for the purpose of determining first experimentally the e.m.f. of the combination and then, by difference, the unknown value. The e.m.f. of any half-cell does not depend on what other half-cell it is coupled with but is dependent on the temperature and on the concentrations of its components. The normal electrode potential E°_{Cu} of pure copper in a normal solution of cupric ions is -0.34volts $_{Cu}$ corresponding to the partial reaction.



for which $\Delta G^\circ = 15390 \text{ cal.}$, but this value is different if (a) the copper is impure (b) the solution has a concentration (or activity) different from the standard normal concentration or (c) if the temperature is other than $25^\circ C$.

In this case

$$E_{Cu} = E^\circ_{Cu} - \frac{RT}{n} \ln \frac{a_{Cu^{2+}}}{a_{Cu}} \quad (9)$$

so that E_{Cu} becomes less negative on dilution.

It is more common in electro-technology to quote Standard Electrode Potentials as the negative of the values calculated from ΔG° , so that for Cu is + 0.34 volts. This is the voltage which must be applied to balance the reaction. Equation (7) becomes

$$E = E^\circ + \frac{RT}{n} \ln a_i \quad (10)$$

Table 1 of the section on General Aspects of Hydrometallurgy lists Standard Electrode Potentials E° as applicable to Equation (10). As stated there the values of E° are reduction potentials and apply to equations like (2).

ELECTROLYTIC CELL VOLTAGE

The actual voltage necessary to operate an electrolytic cell may be expressed as the sum of five components.

Reaction voltage

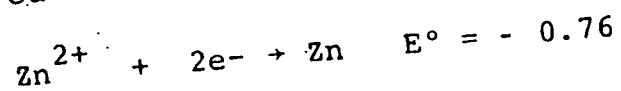
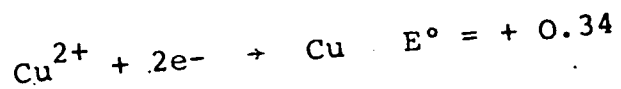
1. The e.m.f. for the net chemical reaction may be calculated for the free energy change for the net reaction and values of the activities (generally approximated by concentrations) of reactants and products - Equation (6).

Alternatively the reaction may be considered as two half electrode reactions and according to the I.U.P.A.C. convention,

$$E_R = E_{\text{cathode}} - E_{\text{anode}} \quad (11)$$

A positive value indicates a spontaneous reaction (voltaic cell) and a negative one will require an applied external voltage.

Thus for reaction (3) under standard conditions



If the copper is to be the cathode,

$$E_R = (+0.34) - (-0.76)$$

and the reactions with copper as cathode and zinc as anode will be spontaneous.

Example: Calculate the e.m.f. of a cell made up of a metallic zinc electrode in a solution with Zn ion activity 10^{-2} connected appropriately to an electrode of metallic copper in a solution of copper ion activity 10^{-3} .

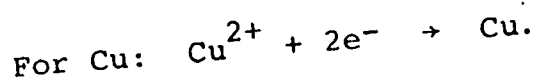
As the reaction in the cell proceeds, is the copper ion activity decreasing or increasing?

Refer to Figure 2.

$$A_{\text{Zn}^{2+}} = 10^{-2}, \quad A_{\text{Cu}^{2+}} = 10^{-3}$$

Apply equation (10) for the reduction potentials:-

$$E = E^\circ + \frac{RT}{nF} \ln a_i$$



$$E_{\text{Cu}} = +0.34 + \frac{RT}{nF} \ln \frac{a_{\text{Cu}^{2+}}}{a_{\text{Cu}}}$$

$$\begin{aligned} \text{Now, } R &= 8.32 \text{ volt coulombs/} (^\circ\text{C}) (\text{mole}) \\ &= 96,500 \text{ coulombs/g equivalent} \end{aligned}$$

$$n = 2$$

and T is assumed to be 298°K .

$$\text{Hence } E_{\text{Cu}} = 0.34 + \frac{0.059}{2} \log_{10} A_{\text{Cu}^{2+}}$$

because the activity of pure copper is unity.

$$E_{\text{Cu}} = 0.34 + \frac{0.059}{2} \log_{10} 10^{-3}$$

$$= 0.25 \text{ V.}$$

Similarly

$$E_{\text{Zn}} = -0.76 + \frac{0.059}{2} \log_{10} 10^{-2}$$

$$= -0.82 \text{ V.}$$

$$E_{\text{R}} = +1.07 \text{ V.}$$

According to the I.U.P.A.C. convention, then, the reaction will proceed spontaneously with the copper being reduced and the zinc being oxidized as the anode. The application of -1.07 V. from an external source would bring the cell into equilibrium and no net reaction would occur. While the application of more than this external voltage would bring about the deposition of zinc and solution of Cu.

Since copper is deposited from solution the activity will decrease.

At equilibrium, $E_{\text{cell}} = 0$.

$$E_{\text{anode}} = E_{\text{cathode}}$$

$$-0.76 + \frac{0.059}{2} \log A_{\text{Zn}}^{2+} = +0.34 + \frac{0.059}{2} \log A_{\text{Cu}}^{2+}$$

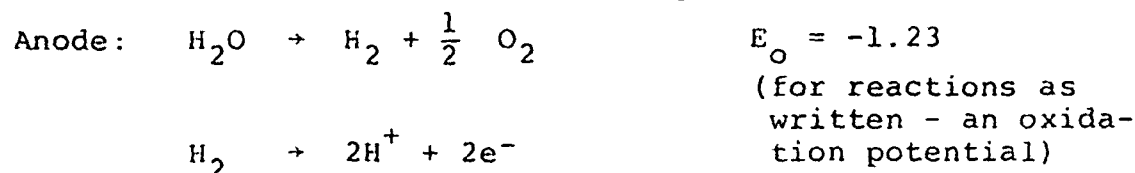
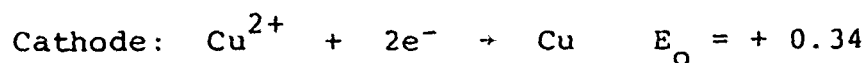
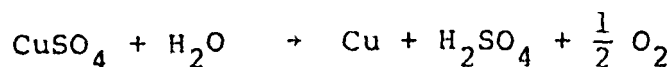
$$\frac{A_{\text{Zn}}^{2+}}{A_{\text{Cu}}^{2+}} = 37$$

which may be compared with the initial ratio of $10^{-2}/10^{-3} = 10$.

2. and 3. Polarization Voltages. These are voltages E_{A} and E_{C}

due to polarization at the anode and cathode respectively. That at the cathode in the above example is due to the concentration

gradient of Cu^{2+} ions caused by their depletion in the solution near the cathode surface. That at the anode is sometimes called oxygen overvoltage if there is some difficulty in nucleating oxygen bubbles as say in the electrolysis of copper sulphate.



$$E_R = - 0.89\text{V}. \quad (12)$$

At the anode there may be a local surplus of H^+ and at the cathode there may be a local surplus of SO_4^{2-} .

These polarization voltages are also known as concentration polarization voltages and can be reduced by agitation or a reducing agent to take up oxygen without the formation of bubbles.

4. Electrolyte resistance. A voltage E_Ω is required to overcome the ohmic resistance of the electrolyte. This can be kept low by adjustment of its composition to ensure a high concentration of conducting ions. It can be kept low by designing the cell so that the electrical paths are wide and short (leaving space for the growth of the cathodes, of course) since, as in solid conductors, resistance R is proportional to the length of the path l and inversely proportional to its cross-sectional area s

i.e.
$$R = r \cdot \frac{l}{s}$$

where r is the specific resistivity of the electrolyte in ohms per cm cube. r depends on the ionic species present and the least contribution is made by hydrogen ions and the next smallest by hydroxyl ions so that low resistivities are most easily obtained in fairly strongly acid or alkaline solutions (in water). These need not be compatible with low values of E_A . E_Ω increases with current in accordance with Ohm's Law.

5. The contact potential E_K at each electrode and in connections between electrodes and bus-bars must be included in the grand total.

Thus the total e.m.f. required in a cell is

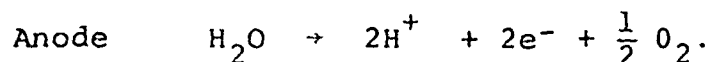
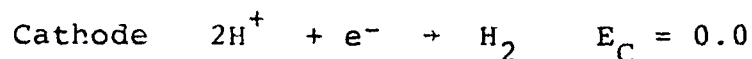
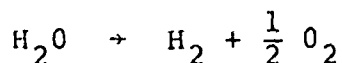
$$E_T = E_R + E_C + E_A + E_\Omega + E_K \quad (13)$$

which may be substantially higher than E_R , perhaps two or three times as high, subject to some control in the design of the cell. In the case of the deposition of copper, for example, a potential drop of about 2.0 might be expected per cell although E_R is only 0.9 volts; and in the extraction

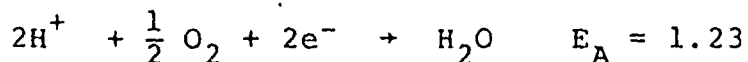
For aluminum the value of E_R is only 1.05 for the net reaction but $E_C \approx 0.45$, $E_A \approx 0.35$, $E_O \approx 2.55$ and $E_K \approx 0.6$ making a total cell e.m.f. of about 5.0 volts.

Faraday's Law is, of course, valid in these operations but it is found that the current used exceeds that theoretically necessary to deposit the metal being extracted and this leads to the term "current efficiency" which is the ratio of the weight of metal actually deposited to that which should have been deposited in accordance with Faraday's Law. The apparent deviation is due to the fact that side reactions occur -- re-solution of the cathode material, as the acid content builds up; deposition of other substances and particularly the simultaneous evolution of hydrogen at the cathode; electrical leakages; and the conversion of electrical energy into heat. This last item is important in processes where the electrolyte is a fused salt as the heat generated (quite deliberately) may be used to keep the electrolyte molten. In such a case, e.g. that of aluminum already mentioned, it is desirable to keep the resistance of the electrolyte up to some minimum value. In other cases supplementary heating is provided.

Electrolytic deposition from aqueous solutions is restricted to those metals whose ions are discharged with a lower cell e.m.f. than is required to discharge hydrogen ions. The net reaction involved in the dissociation of water is

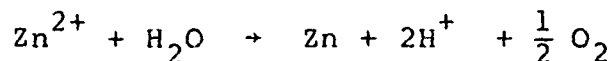


Written as a reduction potential we have



$$\therefore E_R = -1.23v.$$

In the case of the deposition of zinc the net reaction is



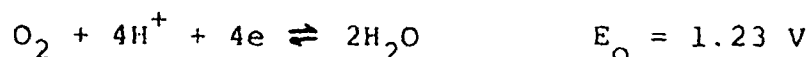
for which

$$\begin{aligned} E_R &= (-0.76) - (1.24) \\ &= -2.00 v. \end{aligned}$$

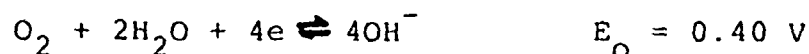
It would, therefore, appear that copper could readily be deposited electrolytically by the application of 0.9 v., but that attempts to deposit zinc by the application of the necessary 2.0 v would lead only to the vigorous evolution of hydrogen and oxygen. Fortunately however, the nucleation and deposition of hydrogen does not occur at the minimum thermodynamic value of E° , for kinetic reasons. In other words, there is a high hydrogen "overpotential" or "overvoltage" by virtue of which the deposition of hydrogen at the cathode is inhibited until the cathode potential is at a much lower value than the arbitrary 0.0 volt assigned to the standard hydrogen electrode, and measurable only when the hydrogen evolution is catalytically assisted by the nature of the platinum black surface of the special electrode. At more normal surfaces, zinc and cadmium, cobalt and nickel, tin and lead can all be deposited in preference to hydrogen despite their inferior positions in the electrochemical series. In practice the cell e.m.f. is usually so much higher than E° that some evolution of hydrogen accompanies deposition of the metal. This should be kept to a minimum by maintaining the cell e.m.f. as low as is practicable and keeping potential catalysts out of the system. (An exceptional case is the deposition of sodium from aqueous solutions on to a mercury cathode. In this case the hydrogen overvoltage on the extremely smooth surface of the liquid metal is very high. At the same time, the activity of sodium in dilute solution in the mercury is very low and the two effects are additive. This phenomenon has industrial applications in the manufacture of caustic soda in the Solvay cell.)

ELECTROWINNING AND ELECTROREFINING

The two processes of electrowinning and electrorefining can be considered together since the cathodic reactions are essentially the same in both processes. In electrowinning the anode is required to be inert so that the electrolyte will not become contaminated during operation and so that the anode will not require frequent replacement. The anodic reaction in electrowinning is primarily the evolution of oxygen. In acid solution the overall reaction is represented by:-



and in alkaline solution by:-



In electrorefining the anode is of course the metal to be refined and so the overall anodic reaction is essentially apart from impurities in the anode the reverse of the cathodic reaction. Clearly in electrowinning, since the electrode reactions are different, there is usually a considerable decomposition potential for the electrolytic process. See Figure 4. The cell voltages in electrowinning commonly have values of 2-5 volts with "energy efficiencies" (expressed as energy consumed per unit weight of material produced) often being 1-1 1/2 kwh/lb of metal. In electrorefining, provided the catholyte and anolyte are of equal strength and temperature, reversible potentials at the electrodes will be the same and the decomposition potential will then be very small. Cell voltages are often less than 0.5 volt and a number of metals are refined for less than 0.25 kwh/lb.

Thus, it can be seen that the values of cell voltages and energy requirements in electrowinning are about five times the corresponding values in electrorefining. This disparity is almost entirely due to the decomposition voltage differences between the two processes and not to widely differing current efficiencies which are usually 80-90% for electrowinning and 90-99% for electrorefining. The current loss is due to leaks and to side reactions. (Current efficiency is defined as the ratio of the amount of metal deposited to the theoretical deposit.)

Metals which cannot be electrolysed from aqueous solution may be deposited from fused salts or "igneous melts". These include aluminum, magnesium, and the alkalis and alkaline earths - all very reactive metals which require some protection from the atmosphere when produced. Metallic aluminum is collected at the cathode at the bottom of the cell and is protected by the electrolyte but in the magnesium process the metal floats on the electrolyte and elaborate cell design is needed to keep the magnesium and the anodic chlorine apart. In the aluminum cell oxygen is released at the carbon anode which reacts forming CO and CO₂ so depolarizing the anode, which is consumed and must be replaced. One means of doing this

continuously is to have an aluminum tube filled with a paste of carbon and tar at the top which bakes hard as it is fed down into the cell. Some plants pre-bake the electrodes. The electrolyte must be easily fused and should contain no metals of lower electrode potential than that of the metal being extracted. The anode and cathode materials must be chosen as refractories, special consideration being given to the avoidance of contamination of the metal. At least part of the heat required in these processes will arise in the electrolyte acting as a resistor and this must be considered when the composition of the electrolyte and the cell dimensions are being chosen.

In electrolytic extraction plants, electrodes are usually arranged in parallel in each tank, while a large number of tanks are arranged in series as indicated schematically in Figure 3. If the potential drop in each cell is 2 volts, then fifty tanks in series can be operated by a 100 volt rectifier. The current must be carried between the cells by heavy copper bus-bars to minimize I^2R losses. Aqueous solutions usually cascade by gravity from one tank to the next in a group, being pumped back to the top tank when it flows out of the lowest. When the concentration becomes critically low part of the solution is returned to the leaching plant and replaced with strong solution, or there may be a continuous purge. No attempt is made to reduce the metal ion concentration to a very low value. Pregnant leaching solution may have to be purified with respect to certain ions before being electrolysed to improve process efficiency or the purity of the product. Temperature, pH, and current density also affect the quality of the cathodic material with respect to composition or physical character. Current densities usually lie in the range 10-100 A/ft². High values tend to give a more irregular deposit. The rate of deposition is proportional to current density but the watt-seconds used is proportional to the square of current density so that the use of high current densities becomes costly. Colloids and gums may be added to aqueous electrolytes to control the physical quality of the metal deposited. It should be dense and coherent rather than loose and spongy, and excessive "treeing" or formation of dendritic growths which tend to cause electrical short-circuiting has to be avoided. Some deposits are never coherent, however, one example being silver which deposits as loose crystals which fall to the bottom of the cell.

In refining processes, the behaviour of the impurities in the anode is important. Metals less noble than the principal metal go into solution with it but may not be deposited with it if the conditions of the cell are well chosen. More noble metals do not enter the solution but fall away as an insoluble anode slime which may be collected in a fabric bag hung round the anode or accumulate in the bottom of the cell. These slimes may contain gold, silver and platinum metals whose values may justify the choice of an overall process which includes electrolytic refinement.

There are some interesting variations in electrolytic technique. In nickel extraction, it is possible to use slabs of nickel sulphide as anodes. The sulphur collects as a large part of the anode slime. Impurities, copper and cobalt, enter the solution along with the nickel but the electrolyte is denied access to the cathode until these have been removed by chemical treatment. The cathode is situated in another compartment immersed in the purified "catholyte" which is in electrolytic contact with the impure "anolyte" only through a diaphragm of canvas. The flow of electrolyte through the interstices of the canvas prevents impurities entering the catholyte.

These cells are called diaphragm cells. In cobalt extraction, deposition from acid solutions is not possible. Cobalt hydroxide is precipitated with lime and the slurry electrolysed. Cobalt is dissolved continuously at the anode and deposited at the cathode, the concentration in the solution always being very low. The refining of aluminum is elegantly performed using a dense solution of the impure metal in copper as the anode, with a less dense electrolyte containing, however, enough barium salt to raise its density above that of the pure aluminum which floats as cathode on top.

Example:

How much copper can be deposited from a CuSO_4 solution by a current of 30 amperes flowing for 8 hours?

Solution:

$$30 \times 3600 \times 8 = 864,000 \text{ coulombs (total)}$$

$$\frac{864,000}{96,500} = 8.95 \text{ faradays}$$

$$\text{But 1 faraday will deposit } \frac{63.57}{2} = 31.8 \text{ g of Cu}$$

$$8.95 \times 31.8 = 284 \text{ g of Cu deposited (at 100\% current efficiency)}$$

Example:

The following data apply to an electrolytic extraction operation for producing copper. Electrolyte CuSO_4 ; cathode, copper sheets; lead anodes; average resistivity of electrolyte 5.6 ohms per cubic centimeter, electrodes 4.2 cm apart; current density 175 amperes per square meter; gas overvoltage 0.48 volt; voltage drop cathode to busbar 0.06 volt, and anode to busbar 0.12 volt. Current efficiency 90 per cent; 1000 amperes current per tank.

Required:

- (i) The voltage drop due to ohmic resistance of electrolyte.
- (ii) The decomposition voltage.
- (iii) Voltage drop, anode to cathode.
- (iv) Voltage drop, busbar to busbar.
- (v) Weight of copper deposited per day per tank.
- (vi) Kilowatts used per tank.
- (vii) Kilowatt-hours per kilogram of copper deposited.

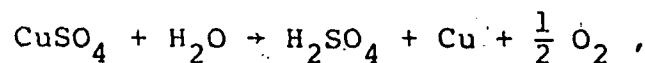
Solution:

$r = 5.6$, $l = 4.2$, $s = 10,000$ sq cm (1 sq m), and $I = 175$ amperes

$$R = r \frac{l}{s} = 5.6 \times \frac{4.2}{10,000} = 0.00235 \text{ ohm}$$

$$E_{\Omega} = IR = 175 \times 0.00235 = 0.41 \text{ volt} \quad \dots \dots \dots (i)$$

As found above, Equation (12), for the reaction



$$E_R = -0.89 \text{ volts} \quad \dots \dots \dots (ii)$$

(This is for the reactants and products in standard condition. Corrections can, of course, be made.)

$$\begin{aligned} E_T - E_K &= E_R + E_{\Omega} + E_A + E_C \\ &= 0.89 + 0.41 + 0.48 \\ &= 1.78 \text{ volts} \quad \dots \dots \dots (iii) \end{aligned}$$

(Here the sign of E_R is ignored since it is realised that all the inefficiencies will serve to increase the necessary e.m.f.)

$$\begin{aligned} E_T &= 1.78 + 0.06 = 0.12 \\ &= 1.96 \quad \dots \dots \dots (iv) \end{aligned}$$

kgCu per day per tank

$$\begin{aligned} &= \frac{0.9 \times 1000 \times 3600 \times 24}{96500} \times \frac{63.6}{2} \times \frac{1}{1000} \\ &= 25.6 \quad \dots \dots \dots (v) \end{aligned}$$

$$\begin{aligned} \text{kw per tank} &= 1000 \times 1.96w = 1.96 \text{ kw} && \dots \dots \dots \text{(vi)} \\ \text{kwh per tank per day} &= 1.96 \times 24 \\ &= 47.0 && \dots \dots \dots \text{(vii)} \\ \text{kwh per kgCu} &= \frac{47.0}{25.6} = 1.84 && \dots \dots \dots \text{(viii)}. \end{aligned}$$

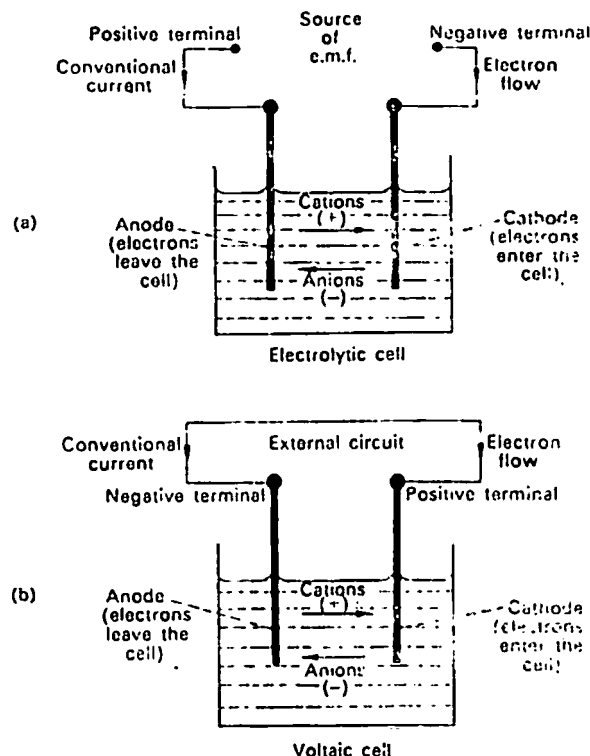


FIG. 1 : ELECTRODE TERMINOLOGY FOR ELECTROLYTIC AND VOLTAIC CELLS

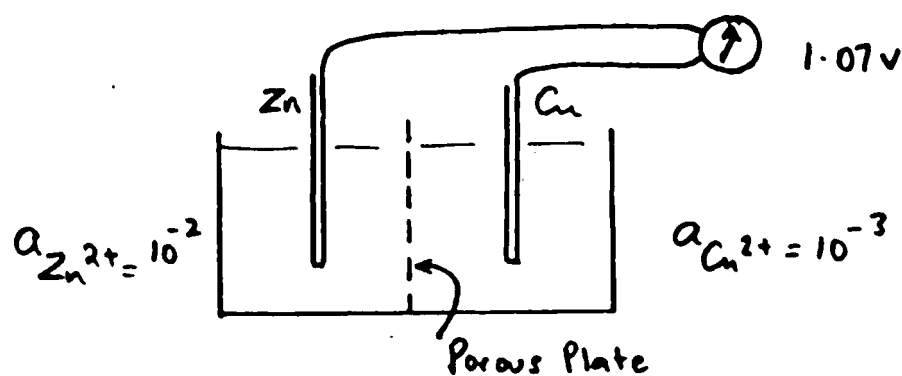


FIG. 2: DANIELL CELL

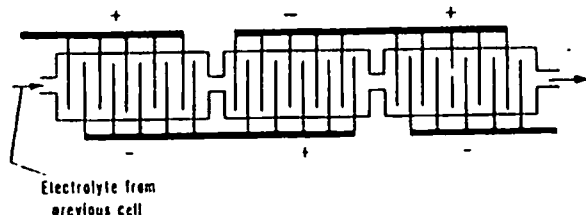


FIG. 3: The arrangement of electrodes in an electrolytic extraction plant is parallel within each cell, but cells are arranged in series.

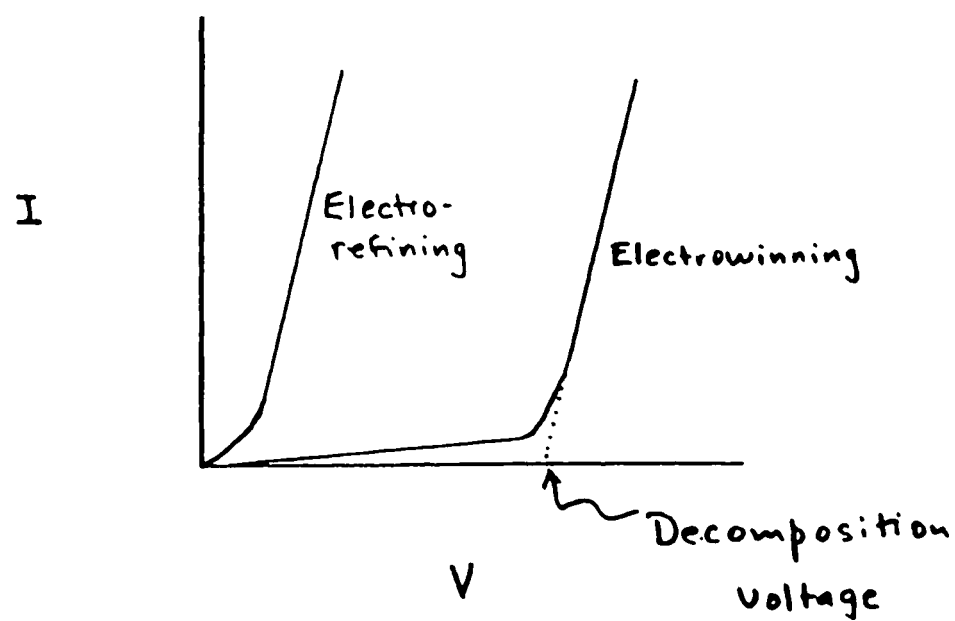


FIG. 4 CURRENT - VOLTAGE CHARACTERISTICS OF
ELECTROLYTIC CELLS

first

~~first~~

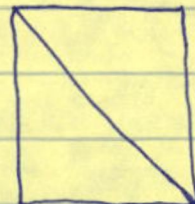
Carbon Au, Ag, Cu

absorb metal cyanide complex
plus free cyanide

Strip off Carbon

w/ hot Caustic

(CN soln for Zn, Cu, etc)



Electrowin on Cathodes

(SS Wool)

pH electrowin sol'n

35 #/T Caustic electrolyte 2-4%

↳ pH 14

$CN \rightarrow NH_3, NO_3, NO_2$. free CN^-

Bob Polak

Dan Blakeman

Mike Frist

free ions to Electrowin